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Title: POROSIMETRIC STUDY OF CATALYST LAYER OF POLYMER ELECTROLYTE FUEL CELL (PEFC)

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Porosimetric Study of the Catalyst Layer of Polymer Electrolyte Fuel Cells

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Introduction

The cathode in a polymer electrolyte fuel cell (PEFC) contributes the largest energy loss due to the slow kinetics of the oxygen reduction reaction (ORR). This issue can be addressed by either developing new noble catalysts for the ORR or increasing catalyst utilization. One effective way to increase catalyst utilization is to increase the pore volume and porosity of the catalyst layer so that the catalyst clusters are maximally exposed to gas reactants. Here, we report our study on the porosimetry of the cathode catalyst layer made with the ultra-thin film catalyst layer technique which was developed by Mahlon Wilson [1] in our group, the effect of the making process of this membrane electrode assembly (MEA) on the porosimetric profile of catalyst layers, and the correlation of the porosimetry with the performance of the catalyst layers.

Experimental

The Catalyst layer was prepared by the so called "decal process"[1,2]. It is worth pointing out that special attention is needed for sample preparation, because the porosimetry of a catalyst layer depends on the type of catalyst used. The anode and cathode catalyst layers, which were hot pressed on two sides of the Nafion membrane, must be of the same catalyst. Otherwise, the measured porosimetric data will be the average of the two different catalyst layers. Mercury porosimeter was used because of its wide range of pore size, from 2 to 1000 nm in pore diameter, and well-established theory for data interpretation.

Results and Discussions

It was found that with the same composition, making procedure, and parameters, the porosimetry of the catalyst layers is different with different catalysts used, namely, the porosimetry of catalyst layers is dependent on the type of the catalyst. This may be due to the different surface polarities of catalysts and the alternation of the surface properties of carbon support, such as surface tension, wetting ability, and polarity, after these different noble metal catalyst have been loaded on carbon support, in which either precious metal basic salts or acidic salts are used. Another interesting phenomenon is that the boiling process in the MEA-making significantly increases pore volume and porosity of catalyst layers. There is a huge difference in pore volume and porosity of the catalyst layer before and after boiling. The boiling of the catalyst layer swells both the recast Nafion network within the catalyst layer and the Nafion membrane, and the subsequent drying of the catalyst layer on a vacuum table makes both the recast Nafion network and membrane contract.

The expansion and contraction of the Nafion membrane and recast Nafion network create more void space inside the catalyst layer and are responsible for the increase of porosity of the catalyst layer after boiling. The Nafion ionomer is a major component in the catalyst layer, serving both as the binder to hold the catalyst/carbon clusters together to form a porous layer and as the proton conductor. The porosimetry of the catalyst layers varies with the Nafion ionomer content, which is shown in Figure 1. It is noticed that the majority of pore sizes concentrates in the range of 3.8 to 5.6 nm in diameter for catalyst layers with 28 and 33 wt. % Nafion, respectively. This pore size is much smaller than the primary pore size, which is 20 to 40 nm, as reported by Makoto Uchida et al. [3]. We speculate that such small pore size benefits the ORR because water may exist in the form of vapor phase instead of liquid phase in these tiny pores, which makes the diffusion of oxygen much faster than in liquid water. This may be one of the explanations for the best performance achieved by the catalyst layer with 28 wt. % Nafion. The removal of the Nafion ionomer skin on the surface of the catalyst layer greatly increases the pore volume and porosity of the catalyst layer because it removes the gas diffusion and water dissipation barrier made of nafion ionomer and makes the inactive catalyst clusters active by exposing them to reactant gases.

Conclusions

The porosimetry of PEFC catalyst layers is dependent on the catalysts used in the layers. MEA-making process influences the porosimetric profile of a catalyst layer. The correlation of the porosimetric data with the performance of the catalyst layers suggests that Nafion content in catalyst layers plays a vital role on the structure of the catalyst layer, such as in pore size and pore distribution, and further influences the performance of PEFC.

Acknowledgements

References

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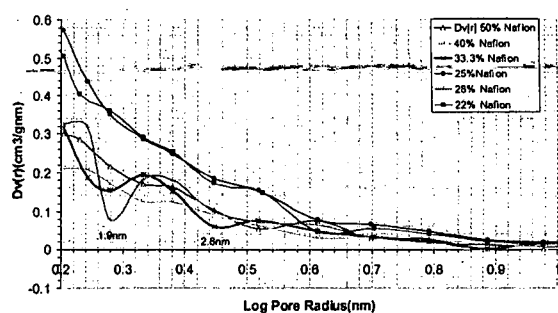

Figure 1. Intrusion curves of Volume pore size distribution of catalyst layers as the function of Nafion content (weight percent).